None of the references cited in the May 24, 2002 Office Action disclose or suggest a method for producing an underwater immersion block.

If the Examiner has any comments, questions, objections or recommendations, the Examiner is invited to telephone the undersigned at the telephone number given below for prompt action.

Respectfully submitted,

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- 1 -

(54) [Title of the Invention]
Pavement block and method for manufacturing same

(57) [Abstract]
[Object]
The object is to provide a cement-base pavement block having high surface hardness, excellent abrasion resistance, and excellent resistance to foxing and crocking, and to provide a method for manufacturing thereof.

[Constitution]
A first layer 3 formed by kneading a binder of a mixture of one or more of calcium-base cement, hydrated lime, granulated blast furnace slag, and the like, with a coarse aggregate 2a and water, and a second layer 4 formed by kneading a binder of a mixture of one or more of calcium-base cement, hydrated lime, granulated blast furnace slag, and the like, with a fine aggregate 2b, a pigment, and water, are layered to each other to form a specified form shape. The form shape is exposed to a carbon dioxide gas atmosphere and is subjected to carbonation-curing to form a carbonated hard layer 5 on the surface of the form shape within 72 hours from the formation of the form shape 1.
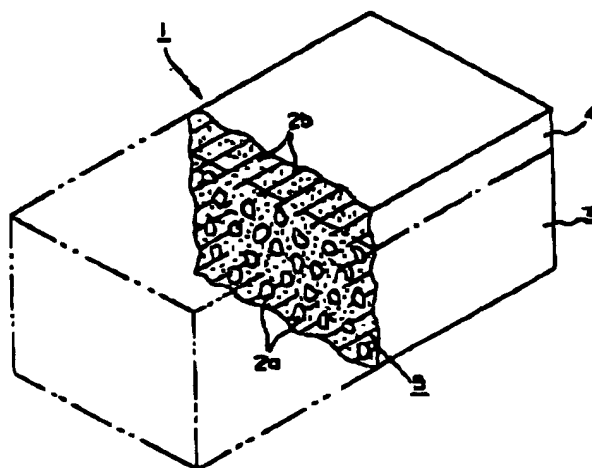
1 :	Form shape
2a :	Coarse aggregate
2b :	Fine aggregate
3 :	First layer
4 :	Second layer
5 :	Hard layer

[Claims]

1. A pavement block comprising: a first layer formed by kneading a binder of a mixture of one or more of calcium-base cement, hydrated lime, and granulated blast furnace slag, with a coarse aggregate and water; a second layer formed by kneading a binder of a mixture of one or more of calcium-base cement, hydrated lime, and granulated blast furnace slag, with a fine aggregate, a pigment, and water, which second layer being layered on the first layer, which layered body of the first and second layers is formed into a specified form shape; and a carbonated hard layer being formed at the surface of the form shape by exposing the form shape to a carbon dioxide gas atmosphere and by conducting carbonation-curing thereof within 72 hours from the formation of the form shape.

2. A method for manufacturing pavement block comprising the steps of: forming a first layer by pouring a specified amount of a kneaded mixture of one or more of calcium-base cement, hydrated lime, and granulated blast furnace slag, with a coarse aggregate and water, into a form; forming a second layer by pouring a specified amount of a kneaded mixture of one or more of calcium-base cement, hydrated lime, and granulated blast furnace slag, with a fine aggregate, a pigment, and water, onto the first layer in the form; applying vibratory compaction to the layered mixture followed by taking out the two-layered form shape from the form; and forming a carbonated hard layer at the surface of the form shape by exposing the form shape to a carbon dioxide gas atmosphere and by conducting carbonation-curing to form the surface carbonated hard layer within 72 hours from the formation of the form shape.

[Detailed Description of the Invention]
[0001]
[Field of the Invention]
The present invention relates to a cement-base pavement block used for pavement of footway, park, parking lot, roadway, and the like, and to a method for manufacturing thereof.

[0002]
[Description of Prior Art]
Pavement blocks (interlocking blocks) are widely used for the

pavement of footway, park, and the like responding to the increasing requirements to the urban view. The pavement blocks are roughly grouped into three categories: cement-base, ceramic-base, and resin-base. As of these, cement-base pavement blocks are widely applied owing to the superiority in cost and in freedom of shaping. Conventional cement-base pavement blocks are manufactured by kneading cement as the binder, with a pigment and water, by forming them into a specific shape, and by curing the shape in a curing chamber or in a seat of PVC or the like until the cement fully undergoes the hydration reaction, (for example, the one disclosed in JP-B-4-16561, (the term "JP-B" referred herein signifies the "examined Japanese patent publication")).

[0003]
[Problems to be Solved by the Invention]

The cement-base pavement blocks are widely used owing to their superiority in shape freedom and in cost. They have, however, a disadvantage of low abrasion resistance on the surface thereof, and they easily wear.

[0004]

To this point, as the hardening technology of cement and other materials, several methods have been introduced, such as a high strength hardened body (JP-A-4-349161, (the term "JP-A" referred herein signifies the "unexamined Japanese patent publication")), a method for improving chemical durability of cement (JP-A-59-88387), and a method for hardening converter slag (JP-A-56-38549). With those methods, there arise problems of color changes caused by efflorescence of cement and of discoloration caused by surface wear. The phenomenon of efflorescence appears in a situation given below. When cement undergoes the hydration reaction to produce a hydrate consisting of calcium oxide (CaO), silicon oxide (SiO_2), and water (H_2O), (hereinafter the hydrate is referred to as "C-S-H"), the amount of CaO in the cement is excessive to the amount of SiO_2, so the surplus CaO becomes calcium hydroxide($Ca(OH)_2$) along with the progress of the hydration reaction, and the calcium hydroxide ($Ca(OH)_2$) deposits on the surface of the block, which whitens the block. To prevent the efflorescence, it is known to prevent the deposition of the surplus $Ca(OH)_2$ on the surface. There is, however, no effective means to prevent efflorescence other than the method of applying resin on the surface. Since the resin coating

is expensive, the method is not generally adopted.

[0005]

An object of the present invention is to provide a cement-base pavement block that has high surface hardness and that has excellent abrasion resistance and excellent resistance to foxing and crocking, and to provide a method for manufacture thereof.

[0006]

[Means to Solve the Problems]

The pavement block according to the present invention has: a first layer formed by kneading a binder of a mixture of one or more of calcium-base cement, hydrated lime, granulated blast furnace slag, and the like, with a coarse aggregate and water; a second layer formed by kneading a binder of a mixture of one or more of calcium-base cement, hydrated lime, granulated blast furnace slag, and the like, with a fine aggregate, a pigment, and water, which second layer being layered on the first layer, and which layered body of the first and second layers is formed into a specified form shape; and a carbonated hard layer being formed at the surface of the form shape by exposing the form shape to a carbon dioxide gas atmosphere and by conducting carbonation-curing thereof within 72 hours from the formation of the form shape.

[0007]

The method for manufacturing the pavement block according to the present invention contains the steps of: forming a first layer by pouring a specified amount of a kneaded mixture of one or more of calcium-base cement, hydrated lime, granulated blast furnace slag, and the like, with a coarse aggregate and water, into a form; forming a second layer by pouring a specified amount of a kneaded mixture of one or more of calcium-base cement, hydrated lime, granulated blast furnace slag, and the like, with a fine aggregate and water, onto the first layer in the form; applying vibratory compaction to the layered mixture followed by taking out the two-layered form shape from the form; and forming a carbonated hard layer at the surface of the form shape by exposing the taken out form shape to a carbon dioxide gas atmosphere thus conducting carbonation-curing within 72 hours from taking out the form shape.

[0008]

[Constitution]

According to the present invention, the pavement block is manufactured by: forming a first layer by pouring a specified amount of a kneaded mixture of one or more of calcium-base cement, hydrated lime, granulated blast furnace slag, and the like, with a coarse aggregate and water, into a form; forming a second layer by pouring a specified amount of a kneaded mixture of one or more of calcium-base cement, hydrated lime, granulated blast furnace slag, and the like, with a fine aggregate, a pigment, and water, onto the first layer in the form; applying vibratory compaction to the layered mixture followed by taking out the two-layered form shape from the form; and forming a carbonated hard layer at the surface of the form shape by exposing the taken out form shape to a carbon dioxide gas atmosphere within 72 hours from taking out the form shape, thus conducting carbonation-curing. Accordingly, the calcium oxide (CaO) existed in the binder is converted to the calcium carbonate ($CaCO_3$) starting from the surface of the form shape, and the calcium carbonate ($CaCO_3$) functions as a binding agent to form a hard layer. Most of the binder after the carbonation reaction becomes $CaCO_3$ and silicon oxide gel (SiO_2 gel), so the efflorescence phenomenon occurs very little, and the resistance to foxing and crocking improves.

[0009]

Since the CaO existed in the binder is converted to $CaCO_3$ starting from the surface of the form shape to form the hard layer, the amount of calcium hydroxide ($Ca(OH)_2$) which is deposited by the surplus CaO inside the form shape is very slight to the total form shape. Furthermore, the deposited $Ca(OH)_2$ is prevented by the surface hard layer made of $CaCO_3$ from releasing to outside. The $Ca(OH)_2$ which is prevented from releasing to outside forms a hard layer around the aggregate inside of the form shape. The $Ca(OH)_2$ is a hard mineral compared with C-S-H, and contributes to the increase in hardness within the form shape.

[0010]

Since the pigment is mixed with the binder and is fixed therein, when the binder is converted to a hard one, the adhesiveness of the binder increases. Furthermore, the hard layer formed by $CaCO_3$ is harder than and is superior in abrasion resistance to the C-S-H, so the abrasion

resistance of the carbonated form shape increases.

[0011]
[Examples]

The present invention is described below by the examples referring to the drawings.

Fig. 1 shows a perspective view of a pavement block relating to an example of the present invention, illustrating the structure on a vertical section at longitudinal center part thereof. Fig. 2 is a schematic drawing of enlarged view of a carbonated portion of the form shape of Fig. 1. Fig. 3 through Fig. 8 illustrate the manufacturing process of the block. In Fig. 1, the reference number 1 designates a carbonated and cured form shape that structures the pavement block of the example, having a square pillar shape with 8 cm in height, 11 cm in width, and 22 cm in length. Generally, the form shape 1 is structured by: a first layer 3 made of a mixture of calcium-base cement such as normal cement and white cement, with a coarse aggregate 2a such as crushed stone having 6 to 7 grades, river sand, blast furnace slag, and concrete waste; and a second layer 4 formed on and integrated to the first layer 3, made of a mixture of calcium-base cement similar with that in the first layer 3, a fine aggregate 2b such as river sand of about 0.8 mm in size, and a pigment such as red iron oxide; further a hard layer 5 (hatched portion in the drawing) having several centimeters of thickness, formed at the surface of the formed shape by carbonation-curing.

[0012]

As shown in Fig. 2, the hard layer 5 is formed by covering, for example, the cement 6 around the aggregate 2 with the $CaCO_3$ coating 7 having thicknesses of about 0.3 to 0.5 mm, in a form of egg-shell, while these components are binding to each other.

[0013]

Detail description of the preparation of the structure along the manufacturing steps is given below. The calcium-base cement 8 such as normal cement and white cement, the coarse aggregate 2a, and water are mixed and kneaded. The mixture is poured into the form 9 to a specified amount to form the first layer 3, (Fig. 3, Fig. 4). The calcium-base cement 8 similar with that of the first layer 3, the fine aggregate

2b, the pigment, and water are mixed and kneaded. The mixture is poured onto the first layer 3 in the form 9 by a specified amount to form the second layer 4, (Fig. 5, Fig. 6). Vibratory compaction is given to the layers 3 and 4, and then ordinary curing is applied to the mixture within 72 hours after the compaction and for a period that the form shape in the form 9 can maintain the shape. When the form shape 1a under the progress of curing by hydration reaction becomes to keep the shape, the form shape 1a is taken out from the form 9, and is transferred to the container 10, (Fig. 7). The transferred form shape 1a is exposed to the carbon dioxide gas atmosphere 11 at 10°C to 99°C of temperature and 10 to 100 vol.% of CO_2 content for 30 minutes to 72 hours, (the action is called the "carbonation-curing"). With the carbonation-curing, when the hard layer 5 is formed on the surface of the form shape 1a by several centimeters of thickness after the carbonation-curing, thus forming the form shape 1, (Fig. 8), the form shape 1 is taken out from the container 10. The time of carbonation-curing (30 minutes to 72 hours) necessary to form the hard layer 5 having several centimeters of thickness at the surface of the form shape is experimentally determined for each type of form shape, in advance. Thus, after the time for carbonation-curing determined for each type of form shape has passed, the hard layer 5 is assumed to be formed. The carbonation-curing is not necessarily conducted in the container 10, and the operation may be given in a room, under a seat such as PVC, or outdoors if only the specified atmospheric condition such as carbon dioxide gas concentration and temperature is assured for a necessary period.

[0014]
Regarding the pavement block according to the present invention, which is manufactured by the above-described method, the reason that the non-cured form shape 1a is subjected to carbonation reaction within 72 hours is that the CaO existed in the cement has to be converted to $CaCO_3$ before the efflorescence of cement occurs. The efflorescence of cement appears within 3 to 4 days after mixing the cement with water. The effect of suppressing the efflorescence by carbonation is attained before the occurrence of efflorescence. However, if the carbonation is given after generating the efflorescence, the efflorescence is enhanced because the surface $Ca(OH)_2$ is carbonated. Consequently, the period to conduct carbonation-curing is specified to 72 hours or less. The reason that the period between forming and carbonation-curing has

a range is described below. The carbonation-curing may be given immediately after the forming. The carbonation reaction rate, however, strongly depends on the quantity of contained free water, and the maximum quantity of free water is around 15 wt.% (expressed by weight percentage of the quantity of free water to the quantity of cement). The water content is very small compared with general form shape water content (25 to 50 wt.%). Therefore, the carbonation reaction rate is small, which results in very poor production efficiency. However, to attain the block form shape water content of 15 wt.% is difficult and impracticable. To this point, the inventors of the present invention studied to find a method of increasing the carbonation reaction efficiency without varying the conventional production process, and found a new phenomenon that the reduction in the quantity of free water increases the carbonation reaction rate because the hydration reaction of the cement makes the form shape water fix to decrease the amount of free water. Based on the finding, the period of hydration for the carbonation-curing is specified within 72 hours that do not induce efflorescence, depending on the quantity of form shape water content.

[0015]

Since the carbon dioxide gas concentration gives significant influence on the reaction rate, higher concentration thereof is more preferable. In view of cost, however, high concentration gas is expensive. To this point, the inventors of the present invention studied the carbon dioxide gas concentration with the curing time aiming at the utilization of general flue gas. As shown in Table 1, even around 5 vol.% of carbon dioxide gas gives satisfactory effect on the suppression of efflorescence and on the hardening of surface layer. The concentration of carbon dioxide gas of 10 vol.% or above is more preferable. Consequently, the concentration of carbon dioxide gas is specified to a range of from 10 to 100 vol.%. The term vol.% signifies volumetric percentage.

[0016]

[Table 1]

Concentration of carbon dioxide gas (vol.%)	a *	b *	L *	Metric chroma (c *)	Lightness difference (△L *)	Wear (sand drop test) g
0	10.78	7.19	43.24	12.96	Reference	78
1	10.91	7.14	42.22	13.04	1.02	76
2	11.08	8.44	42.18	13.93	1.06	81
3	11.98	7.32	40.94	14.04	2.30	73
5	11.74	9.28	37.98	14.97	5.26	67
8	19.02	8.18	37.17	15.38	6.07	69
10	12.76	8.11	36.42	15.12	6.82	54
15	12.39	9.04	36.42	15.34	6.82	58
20	12.10	8.81	35.83	14.97	7.41	58
30	13.68	7.74	36.27	15.72	6.97	59
40	13.41	8.89	36.12	16.09	7.12	42
50	14.33	6.98	33.96	15.94	9.28	48
60	14.71	7.78	34.05	16.59	9.19	51
100	14.68	8.73	34.98	16.90	8.26	46

[0017]

The symbol $\triangle L*$ in Table 1 designates the difference in lightness on the sample relative to the standard value of lightness of sample at zero content of carbon dioxide gas. Table 1 gives examples of observed values of the metric chroma ($c* = (a*^2 + b*^2)^{1/2}$), the lightness $L*$, and the wear (sand drop test) against the content of carbon dioxide gas. The conditions of observation were: the pigment added to the second layer being colored to red using red ion oxide; the mixing ratio of water to cement (w/c) being 30 wt.%; the curing time before carbonation-curing being 24 hours; and the curing time for carbonation-curing being 24 hours. The curing time before carbonation-curing is a normal curing time after the form shape 1a is taken out from the form 9. Determination of the metric chroma ($c* = (a*^2 + b*^2)^{1/2}$), the brightness $L*$, and the wear (sand drop test), were conducted conforming to the methods described below.

[0018]

Evaluation of the efflorescence resistance and the resistance to

foxing and crocking of sample was given by determining the spectral reflectance factor R (λ) of the sample conforming to the method specified in JIS Z8722 "Methods of colour measurement". That is, the sample was illuminated from all directions to let a spectrophotometer receive the reflection light at an angle of 8º to normal direction to the sample plane, thus deriving the spectral reflectance factor R (λ) of the sample. The applied light source was D_{65} light source specified in JIS Z8720. Based on thus determined spectral reflectance factor R (λ), the tristimulus values of object color, X, Y, and Z, and the values of x, y, and z in the XYZ colorimetric system were calculated by the formula 1 given below conforming to the method specified in JIS Z8701 "Colour specification - The CIE 1931 standard calorimetric system and the CIE 1964 supplementary standard colorimetric system", thus numeral expression of object color was given.

[0019]
[Formula 1]

$$X = K \int_{380}^{780} S(\lambda) \, \overline{x}(\lambda) \, R(\lambda) \, d\lambda$$

$$Y = K \int_{380}^{780} S(\lambda) \, \overline{y}(\lambda) \, R(\lambda) \, d\lambda$$

$$Z = K \int_{380}^{780} S(\lambda) \, \overline{z}(\lambda) \, R(\lambda) \, d\lambda$$

$$K = \frac{100}{\int_{380}^{780} S(\lambda) \, \overline{y}(\lambda) \, d\lambda}$$

where, $S(\lambda)$ is the spectral distribution of standard light used in the color specification, $x(\lambda)$, $y(\lambda)$, and $z(\lambda)$ are respective color-matching functions in the XYZ colorimetric system; and $R(\lambda)$ is the spectral reflectance factor.

The Y in the tristimulus values of the XYZ colorimetric system is the value of the luminous spectral reflectance factor expressed by percentage.

[0020]

Furthermore, based on the tristimulus values X, Y, and Z of object color, for the reflection light of the sample, the object color of the sample was expressed by the L*a*b* colorimetric system which is specified in JIS Z8729 "Colour specification - CIE LAB and CIE LUV colour spaces". According to JIS Z8729, the values of L*, a*, and b* are calculated by the formula 2 and the formula 3.

$$L* = 116(Y/Yn)^{1/3} - 16$$

[0021]
[Formula 2]

$$Y/Yn > 0.008856$$

where, Y is the value in the tristimulus value of the XYZ colorimetric system; and Yn is the Y value of standard light on the perfect diffusion and reflection plane.

$$a* = 500[(X/Xn)^{1/3} - (Y/Yn)^{1/3}]$$
$$b* = 200[(Y/Yn)^{1/3} - (Z/Zn)^{1/3}]$$

[0022]
[Formula 3]

$$X/Xn > 0.008856$$
$$Y/Yn > 0.008856$$
$$Z/Zn > 0.008856$$

where, X, Y, and Z are the tristimulus values in the XYZ colorimetric system; and Xn, Yn, and Zn are the tristimulus values in the XYZ colorimetric system on the perfect diffusion and reflection plane.

[0023]

"Color Technology Handbook", pp118-119, Sachio Murata, Sogo Gijutsu Center, (October 1, 2000) describes the relation between the color name of object color visually recognized and the numerical value of the object color expressed by the L*a*b* colorimetric system. That is, large values of lightness index L* bring the object color toward white, and small values thereof bring the object color toward black. The relation is understood from the relation in object color between the lightness V of the object color specified in JIS Z8102 and the visually recognized object color. In other words, JIS Z8102 specifies that large values of lightness V bring the object color toward white, and small values thereof bring the object color toward black. On the other hand, according to JIS Z8721, increased value of luminous spectral reflectance factor Y increases the value of lightness V. Furthermore, from the relation between the XYZ colorimetric system and the L*a*b* colorimetric system, increased value of L* increases the luminous spectral reflectance factor Y and increases the lightness V. Based on the above-given consideration, the efflorescence resistance of pavement block was evaluated by L*.

[0024]

The resistance to foxing and crocking of pavement block was evaluated by the value of metric chroma $(a^{*2} + b^{*2})^{1/2}$. That is, according to the above-cited Color Technology Handbook, the metric chroma $(a^{*2} + b^{*2})^{1/2}$ has a property of color corresponding to the content of pure color component. Therefore, if the metric chroma $(a^{*2} + b^{*2})^{1/2}$ increases, the content of pure color component increases, and if the metric chroma $(a^{*2} + b^{*2})^{1/2}$ becomes close to zero, the object color becomes close to achromaticity. In other words, a sample that shows large metric chroma $(a^{*2} + b^{*2})^{1/2}$ has superior resistance to foxing and crocking, and, a sample that shows small metric chroma $(a^{*2} + b^{*2})^{1/2}$ gives severe foxing and crocking.

[0025]

The abrasion resistance was evaluated as follows. The apparatus specified in JIS A1452 was applied as the testing apparatus. The testing plane of the sample was held to 45° from horizontal plane. A 10,000 g of abrasive was dropped onto the center of the testing plane from 650 mm above thereof. Then, the mass loss of the sample was determined.

The test was conducted while rotating the sample around the center thereof. The sample applied had dimensions of 8 cm x 11 cm x 22 cm. The abrasive applied was the silicon carbide abrasive 2C specified in JIS R6111, having #36 of size. The drop rate of the abrasive was controlled to 400 ±20 g.

[0026]

Although the temperature is not strictly limited for manufacturing the pavement block according to the present invention, temperatures below 10°C is not favorable because the reaction rate significantly reduces. Temperatures above the water boiling point are not favorable because the evaporation of water results in shortage of water needed in carbonation reaction. Also for humidity, no special limitation is given, and the humidity may be selected depending on the amount of free water in the block and on the curing temperature of the block.

[0027]

Table 2 and Table 3 show the Examples A through I according to the present invention, giving different specification of pavement block to each other, along with the Comparative Examples of conventional block.

[0028]

[Table 2]

		Conventional block	Block A	Block B	Block C	Block D
Surface layer	Cement kg/m³	400	400	400	400	400
	Pigment (red) kg/m³	16	16	16	16	16
	Fine aggregate kg/m³	1800	1800	1800	1800	1800
	Coarse aggregate					
	Water/Cement wt%	30	30	25	25	30
Base layer	Cement kg/m³	350	350	350	350	350
	Pigment (red) kg/m³	920	920	920	920	920
	Fine aggregate kg/m³	910	910	910	910	910
	Water/Cement wt%	30	30	25	25	30
Curing period before carbonation h		---	24	24	70	70
Carbon dioxide gas content (vol.%)		---	20	20	10	10
Carbonation period h		---	48	48	24	24
Efflorescence		Appeared	Not appeared	Not appeared	Not appeared	Not appeared
L*		42.34	35.18	34.22	37.95	32.02
a*		10.78	12.33	14.91	11.19	15.03
b*		7.19	8.63	7.61	9.22	6.53
c*		12.96	15.07	17.11	15.01	16.99
$\triangle$E*		Reference	7.46	9.11	4.84	11.18
Wear (sand drop test) g		78	63	62	59	57

[0029]

[Table 3]

		Conventional block	Block A	Block B	Block C	Block D
Surface layer	Cement kg/m³	400	400	400	400	400
	Pigment (red) kg/m³	16	16	16	16	16
	Fine aggregate kg/m³	1800	1800	1800	1800	1800
	Coarse aggregate					
	Water/Cement wt%	30	30	25	25	30
Base layer	Cement kg/m³	350	350	350	350	350
	Pigment (red) kg/m³	920	920	920	920	920
	Fine aggregate kg/m³	910	910	910	910	910
	Water/Cement wt%	30	30	30	30	30
Curing period before carbonation h		0	24	0	70	70
Carbon dioxide gas content (vol.%)		40	60	40	40	60
Carbonation period h		72	72	72	72	24
Efflorescence		Not appeared	Not appeared	Not appeared	Not appeared	Not appeared
L*		32.35	31.87	33.47	31.25	30.97
a*		14.22	14.52	13.95	14.86	15.01
b*		7.96	7.98	8.24	8.05	7.69
c*		16.48	16.87	16.30	17.13	17.22
ΔE*		10.59	11.15	9.48	18.54	12.14
Wear (sand drop test) g		42	54	59	48	57

[0030]

The values of ΔE* in Table 2 and Table 3 designate the difference in color between blocks of A through I and the conventional block for the L*a*b* colorimetric system specified in JIS Z8730. The values of vol.% in these tables designate the volume percentage, the values of wt.% designate the weight percentage, and the values of h designate the time. The blocks given in Tables 2 and 3 had the second layer made of normal cement colored with red pigment such as red iron oxide, and the blocks examples A through I according to the present invention were subjected to carbonation-curing under respective conditions given in the tables. Tables 2 and 3 show that the carbonation within 72 hours after formed is effective in suppressing the efflorescence and in

improving the resistance to foxing and crocking. The tables also show that the resistance to wear (abrasion resistance) increases by the carbonation.

[0031]
[Effect of the Invention]

As described above, the pavement block according to the present invention is structured by a carbonated hard layer at the surface thereof, which carbonated hard layer being prepared by layering a first layer formed by kneading a binder of a mixture of one or more of calcium-base cement, hydrated lime, granulated blast furnace slag, and the like, with a coarse aggregate and water, and a second layer formed by kneading a binder of a mixture of one or more of calcium-base cement, hydrated lime, granulated blast furnace slag, and the like, with a fine aggregate, a pigment, and water, on the first layer to form a specified form shape, and by exposing the form shape to a carbon dioxide gas atmosphere and by conducting carbonation-curing to form the surface carbonated hard layer within 72 hours from the formation of the form shape. The obtained pavement block has large surface hardness, gives excellent abrasion resistance and excellent resistance to foxing and crocking.

[Brief Description of the Drawings]
[Fig. 1]

Fig. 1 shows a perspective view of a pavement block relating to an example of the present invention, illustrating the structure on a vertical section at longitudinal center part thereof.
[Fig. 2]

Fig. 2 is a schematic drawing of enlarged view of a carbonated portion of the form shape of Fig. 1.
[Fig. 3]

Fig. 3 illustrates the first step of the method for manufacturing pavement block relating to an example according to the present invention.
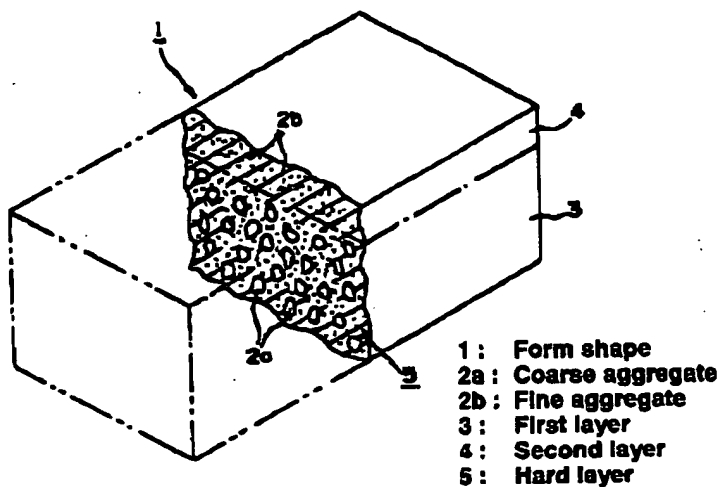[Fig. 4]

Fig. 4 illustrates the first step of the method for manufacturing pavement block relating to an example according to the present invention.
[Fig. 5]

Fig. 5 illustrates the second step of the method for manufacturing

pavement block relating to an example according to the present invention.

[Fig. 6]

Fig. 6 illustrates the second step of the method for manufacturing pavement block relating to an example according to the present invention.

[Fig. 7]

Fig. 7 illustrates the third step of the method for manufacturing pavement block relating to an example according to the present invention.

[Fig. 8]

Fig. 8 illustrates the fourth step of the method for manufacturing pavement block relating to an example according to the present invention.
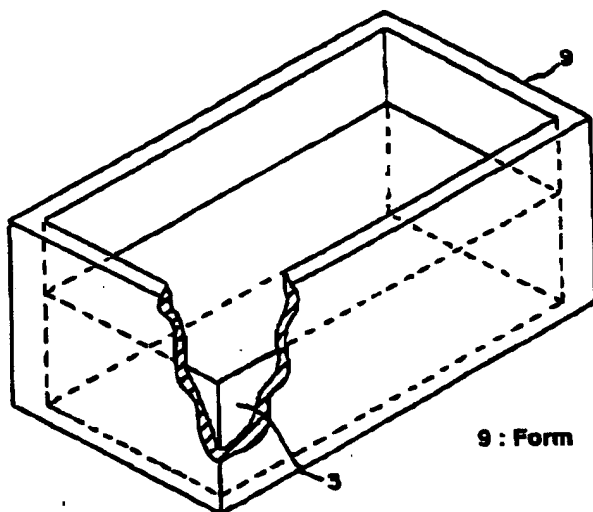
[Description of Reference Numbers]

1, 1a Form shape

2a Coarse aggregate

2b Fine aggregate

3 First layer

4 Second layer

5 Hard layer

8 Binder

9 Form

11 Carbon dioxide gas
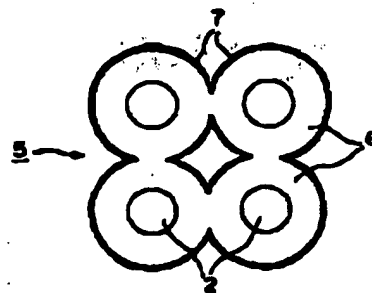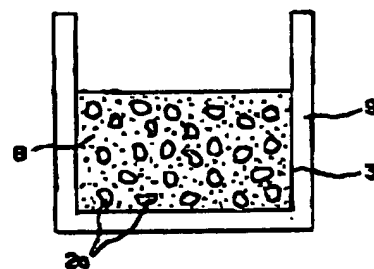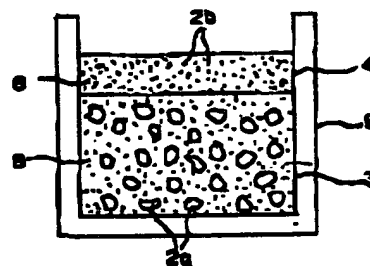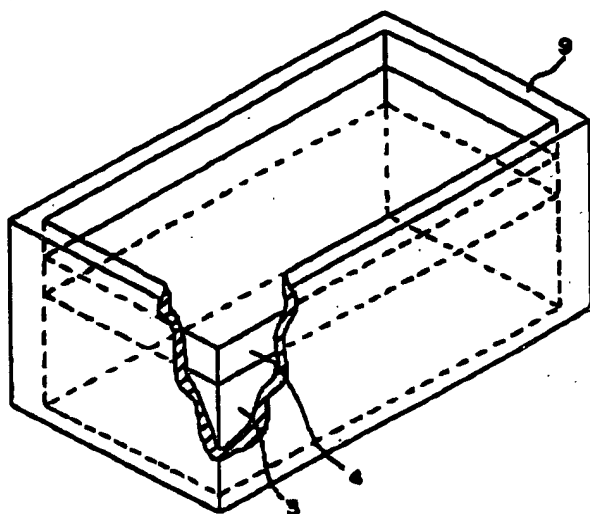
[Fig. 1]

[Fig. 2]

1 : Form shape
2a : Coarse aggregate
2b : Fine aggregate
3 : First layer
4 : Second layer
5 : Hard layer

[Fig. 4]

8 : Binder

[Fig. 3]

9 : Form

[Fig. 6]

[Fig. 5]

[Fig. 7]
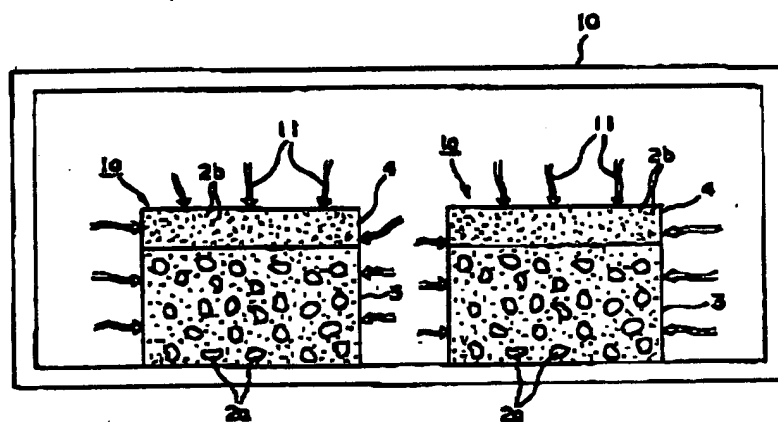
1a : Form shape
11 : Carbon dioxide gas

[Fig. 8]
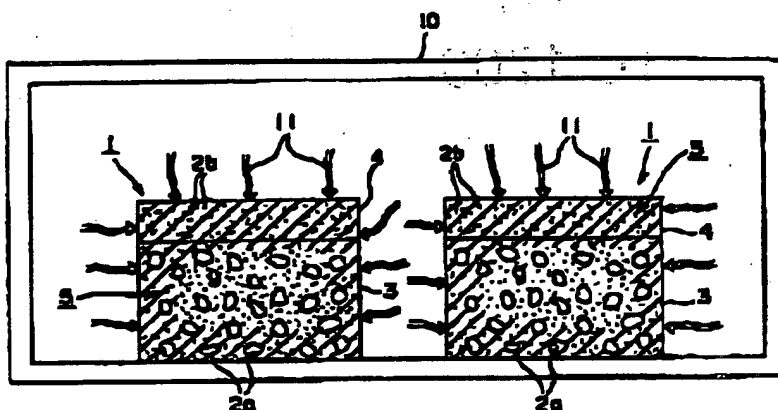
(54) Method for manufacturing civil and architecture material from converter slag

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Specifications

1. Title of the Invention

Method for manufacturing civil and architecture material from converter slag

2. Claim

A method for manufacturing civil and architecture material from slag comprising the steps of: adding K_2CO_3 or Na_2CO_3 by 1 to 30% to a converter slag pulverized to 10 mm or smaller size; further adding water by 5 to 10% to the mixture to kneed them together; pouring the kneaded mixture in a form to conduct forming under forming pressures of from 50 to 150 kg/cm^2; and applying carbonation-curing to the formed shape applying a combustion flue gas for 24 to 94 hours.

3. Detailed Description of the Invention

The present invention relates to a method for manufacturing civil and architecture material using converter slag as the aggregate.

Converter slag generated during converter smelting in the steel making process at iron making works floats on the steel melt at smelting stage, and enters a slag pot after completed the tapping. After being discharged to a slag yard to cool, the slag is pulverized and is used as a material for landfill and other uses.

In recent years, from the point of resource saving, the slag is pulverized to 15 mm or smaller size for reuse as a starting material for sintering or raw material for blast furnace aiming at the utilization of Fe or CaO in the slag, thus effectively using the slag. Since, however, large amount of P exists in slag, as shown in Table 1, and since the P cannot be removed, the content of P increases in the final product, and the remained P gives bad influence on the product performance, thus the reuse of slag has a limitation. Table 2 shows an example of mineral phases in converter slag.

Table 1 Composition of converter slag

SiO$_2$	CaO	Al$_2$O$_3$	FeO	MgO	S	MnO	TiO$_2$	P$_2$O$_5$	free CaO
9 - 20	37 - 59	0.1 - 2.5	5 - 20	0.6 - 8.0	0.06 - 0.3	1.3 - 10.0	0.4 - 0.9	1.5 - 2.3	2 - 6

Table 2 Mineral phases in converter slag

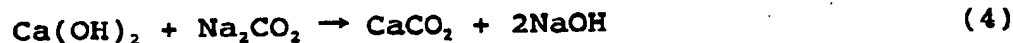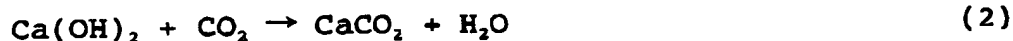| Phase		Content (%)
di-Calcium silicate	β- Ca$_3$ (SiO$_2$, PO$_4$)	30 - 60
tri-Calcium silicate	(Mg, Ca, Mn, Fe)$_3$ SiO$_2$	< 30
Wustite	(Mg, Ca, Mn, Fe)O	10 - 40
Lime	(Mg, Ca, Mn, Fe)O	< 15
di-Calcium ferrite titarate	Ca$_2$ (Al, Fe)$_2$O$_3$ - Ca$_2$Ti$_2$O$_3$	5 - 20

As shown in Table 1 and Table 2, converter slag contains large amount of CaO which is a basic component, further contains non-slagged free CaO component by 2 to 6 %. Accordingly, if the slag is left for a long time, it may swell and collapse. As a result, the converter slag is not positively used in civil and architecture material, though the blast furnace slag has already been used in that material.

The present invention solves the problems of converter slag, and provides a method for manufacturing civil and architecture material from converter slag from the standpoint of resource saving and also of effective use of flue gas at iron making works.

The method for manufacturing civil and architecture material from slag according to the present invention has the steps of: adding K$_2$CO$_3$ or Na$_2$CO$_3$ by 1 to 30% to a converter slag pulverized to 10 mm or smaller size; further adding water by 5 to 10% to the mixture to knead them together; pouring the kneaded mixture in a form to conduct forming under forming pressures of from 50 to 150 kg/cm^2; and applying carbonation-curing to the formed shape applying combustion flue gas for 24 to 94 hours.

The principle of the method according to the present invention is application of the principle of curing CaO component in converter slag using carbonation reaction. That is, the pulverized converter slag is mixed with K$_2$CO$_3$, Na$_2$CO$_3$, and water, then CO$_2$ is blown into the

mixture to initiate the carbonation reaction of Ca components through the reaction formulae (1) through (4):

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (1)$$
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_2 + H_2O \qquad (2)$$
$$Ca(OH)_2 + K_2CO_2 \rightarrow CaCO_2 + 2KOH \qquad (3)$$
$$Ca(OH)_2 + Na_2CO_2 \rightarrow CaCO_2 + 2NaOH \qquad (4)$$

The Co components that contribute to the above-given reactions are, adding to the free CaO, other Ca components such as slagged di-calcium silicate. The produced calcite crystals ($CaCO_3$) become irregular massive crystals. The irregular massive crystals fill the void of slag formed shape to increase the strength of the shape.

When K_2CO_3 and Na_2CO_3 are added to the converter slag conforming to the principle, 1% or larger amount of addition is required to conduct carbonation-solidification of the converter slag. If, however, the added amount of these compounds exceeds 30%, the surplus amount is not necessary for carbonation-solidification, and further the surplus amount thereof decreases the content of converter slag as aggregate, which is not preferable. As for the water to be added to the converter slag, 5 to 10% is required to solidify the converter slag. The pressure for forming is preferably in a range of from 50 to 150 kg/cm^2, which range assures most easy solidification, giving sufficient strength to the formed shape.

Regarding the flue gas used for carbonation of converter slag, it is preferable that the flue gas passes through a water bath or receives water shower spray to reduce the temperature to a degree of not evaporating water content in the formed shape of the converter slag, or to temperatures of 150ºC or below. The flue gas thus treated contains sufficient amount of water and becomes optimum flue gas for carbonation of converter slag.

By curing thus prepared formed shape in a combustion flue gas cooled and humidified for 24 to 96 hours, civil and architecture material products such as high strength blocks having 240 kg/cm^2 or higher compressive strength are obtained.

The compressive strength of hollow block, specified by JIS, is 150 kg/cm^2 to the total cross sectional area. Accordingly, the converter slag block manufactured by the method of the present invention has excellent compressive strength, as described above, and fully

satisfies the JIS specification. As for the acid resistance, the alkali resistance, and the heat resistance, the block manufactured by the method of the present invention gives superior durability to conventional hollow blocks, which superiority is described below.

The flue gas which was used for carbonation-curing of the converter slag formed shape according to the present invention is returned to the original flue gas duct to vent through a stack.

The embodiments of the present invention are described in the following.

A converter slag which composition is shown in Table 3 was pulverized to 10 mm or smaller size. The size distribution is given in Table 4.

Table 3 Composition of converter slag

Cao	SiO_2	MgO	Al_2O_3	MnO	FeO
40.6	9.1	6.7	1.6	6.5	19.7

Table 4 Size distribution of converter slag

Size range (mm)	10 - 5	5 - 2.4	2.4 - 0.8	0.8 - 0.15	0.15 - 0	Water content
Percentage (%)	21	24	19	18	18	9.7

To the converter slag given above, K_2CO_3 was added by the amount of 1%, 10%, and 30%, and Na_2CO_3 was added by the amount of 1%, 10%, and 30%, respectively, and further water was added to each mixture by the amount of 10% by weight. The mixture was kneaded for 20 minutes. Then, the mixture was put into a hollow block forming apparatus to conduct forming under 100 kg/cm² of pressure. After die disjoining, the shape was cured in a low temperature and humidified flue gas.

The applied flue gas was generated from a lime firing furnace, having 300 to 400ºC of temperature. The flue gas passed through water to cool and humidify thereof before use. The property of the flue gas is shown in Table 5.

Table 5 Property of flue gas

CO$_2$	CO	O$_2$	N$_2$	Flue gas temperature
22	3	3	70	95℃

The relation between the curing time under the exposure to flue gas and the compressive strength of the formed shape was evaluated. The result is given in Table 6.

Table 6 Compressive strength

Carbonation time (hr)	K$_2$CO$_3$ content			Na$_2$CO$_3$ content		
	1	10	30	1	10	30
0	2	3	3	3	2	2
8	60	80	105	54	77	110
12	125	146	163	127	144	350
24	250	280	305	245	290	320
48	305	324	346	290	310	366
72	375	396	405	360	370	395
96	426	480	440	405	410	415

The result shows that the converter slag block manufactured by the method of the present invention, which was cured for 24 hours, gave superior compressive strength to the 152 kg/cm^2 of commercially available blocks, and furthermore, longer time of curing provides further increased compressive strength.

Table 7 shows the result of comparative durability test with commercially available blocks.

Table 7 Durability test result

Condition	K₂CO₃ content			Na₂CO₃ content			Commercial block
	1	10	30	1	10	30	
Immersion in tap water for 1 month	355	370	377	345	365	375	145
Immersion in alkaline solution for 1 week	356	365	379	340	355	370	147
Immersion in acidic solution for 1 week	343	349	360	333	342	360	65
Allowing standing in 300ºC atmosphere for 24 hrs	358	390	380	344	370	390	147
Allowing standing in 600ºC atmosphere for 24 hrs	330	377	365	327	336	360	83
Allowing standing in 800ºC atmosphere for 24 hrs	170	190	205	190	180	186	10

The result proves that the converter block manufactured by the method of the present invention has significantly superior durability to that of commercially available blocks.